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The composition of the alignment medium is established as 10-20 ppm (W/V) of parlodion (cellulose nitrate) in distilled amyl acetate. The effect of filter pore-size has been shown to be more significant than previously thought. Fiber losses in the range of 50-80% of total mass are not unlikely, depending on the fiber size distribution. Similarly, ultrasonification has been shown to affect fiber size distribution and subsequent fiber retention by filters. Ambient relative humidity suitable for alignment of single drops has been established to be in the range of 35% to 45% at 22°C to 20°C, respectively. Parameters involved in radio frequency ashing of filters are also discussed. It is shown that ashing quality and subsequent dispersion depends on the fitler membrane, and improves as this concentration is increased.

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INTERIM REPORT: SAMPLE PREPARATION

by

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ABSTRACT

A measurement technique, suitable for submicrogram quantities of asbestos, using a combination of fiber alignment and x-ray diffraction was previously introduced.[1] The x-ray measurement of aligned fibers is a straightforward operation. However, it has since been found that the sample preparation itself depends on several parameters which need critical control.

The composition of the alignment medium is established as 10-20 ppm (W/V) of parlodion (cellulose nitrate) in distilled amyl acetate. The effect of filter pore-size has been shown to be more significant than previously thought. Fiber losses in the range of 50-80% of total mass are not unlikely, depending on the fiber size distribution. Similarly, ultrasonification has been shown to affect fiber size distribution and subsequent fiber retention by filters. Ambient relative humidity suitable for alignment of single drops has been established to be in the range of 35% to 45% at 22° C to 20° C respectively. Parameters involved in radio frequency ashing of filters are also discussed. It is shown that ashing quality and subsequent dispersion depends on the fiber concentration on the surface of the filter membrane, and improves as this concentration is increased.

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1. INTRODUCTION

The feasibility of an x-ray diffraction technique for direct measurement of small masses of asbestos was demonstrated in an earlier report (Ref. 1). The method involved the electrostatic alignment of fibers and embedding them in a thin film for x-ray measurement. The resulting minimum detection limit for pure chrysotile, 0.15 μg, was nearly two orders of magnitude better than previously reported by the usual x-ray diffractometry (Ref. 2). Thus, it showed considerable promise in application to pollution problems - for example, in the analysis of asbestos samples obtained near an emission source.

Following the publication of the feasibility report (Ref. 1), work began on a study of problems associated with the analysis of real samples. It was during the initial stages of this study, that several problems were encountered relative to the parameters involved in the alignment of pure fibers. This work is a description of additional research on sample preparation, which details those difficulties and their remedies. In this report, a brief review of the information covered in Ref. 1 will be presented, followed by an examination of additional parameters which were found to be significant in sample preparation. Finally, suggestions will be offered which are believed to be helpful in alleviating the remaining difficulties.

2. SUMMARY

In the preparation of samples of aligned asbestos fibers by x-ray diffraction, several parameters have been found to be critical. The effects of these parameters on sample preparation are discussed in both qualitative and quantitative terms. Effects of filter pore size, sonication time, radio frequency ashing, ambient humidity and contamination sources are demonstrated.

3. CONCLUSIONS

Preparation of samples of electrostatically aligned asbestos fibers suitable for measurement in a double-detector x-ray diffraction system depends on rigid control of several significant parameters.

The chemical composition of the dispersion/alignment medium has been established as 10-20 ppm (W/V) of parlodion (cellulose nitrate) in distilled amyl acetate.

Filter pore size and ultrasonication have significant effects on fiber retention. Significant fiber loss occurs with smaller fiber size distributions (i.e., by increasing sonication times) and with larger filter pore sizes. The recommended filter pore size is reduced to 0.22 μm. A minimum sonication time dependent on the source of the fibers is emphasized.

Ambient humidity at room temperature has been shown to have a critical influence on fiber alignment. The established range is between 45% at 20°C and 35% at 22°C.

Contamination effects may enter at each stage of sample preparation to affect both dispersion and alignment of fibers. Some contaminations impede the radio frequency ashing of filters while others affect the overall fiber dispersion through production of secondary non-ashable products. In this respect, the use of deionized, but undistilled water in the washing stage has

been correlated with poor dispersion of fibers in amyl acetate-parlodion, whereas no problem seems to arise with deionized, filtered and distilled water.

The most critical step in sample preparation appears to be the radio frequency ashing of filters with small quantities of asbestos, which yields poor dispersion. Preconcentration of filters through the use of smaller filter disks seems to improve the ashing quality but increases the filtration time several fold.

4. RECOMMENDATIONS

The radio-frequency ashing of filters containing only a few micrograms of material should be further investigated. It appears necessary to control the parameters of RF ashing much more rigidly than has been customarily done. For example, the effects of plasma input power, vacuum level, impurity gas mixtures as catalysts should be further studied.

Use of polystyrene-backed cellulose ester filters may prove to be beneficial in reducing the ashed filter residue, through increased mechanical support during ashing. Since the backing itself is not easily ashable, it may be removed from the ash after dispersing the latter in a liquid by mild sonication.

The use of plain (unbacked) filter is recommended for normal situations when the deposit concentration is relatively high. However, with low concentrations it may again prove advantageous to reduce the filtration area as far as practicable in order to increase the surface concentration, and to reduce the quantity of residue ash from the filter.

Finally, since the primary source of the difficulty with RF ashing appears to be the filter membrane itself, the feasibility of eliminating the ashing step (either partially or altogether) should be considered. For example, the filter

collection may be dissolved in an organic solvent, and centrifuged to separate nearly all of the collected solvent (by sonication) and re-centrifuged until only an insignificant level of soluble inorganics remain. One can then determine whether the remaining deposit is readily alignable or whether it requires ashing without the filter membrane to eliminate organic interferences.

5. BRIEF REVIEW OF THE FEASIBILITY REPORT

Calibration standards containing a few micrograms of aligned fibers were prepared in the following way. About 3 mg of chrysotile was sonicated in a 1/2% solution of Aerosol OT in H_2O to produce short straight fibrils. 150 microgram aliquots were filtered through a mixed cellulose ester filter membrane (such as Millipore HAWP). The filter was then ashed in a radio frequency (RF) plasma asher to remove the filter material. The ashed product was dispersed in the "alignment medium", defined as 0.001% parlodion in amyl acetate. A small aliquot of this dispersion, equivalent to about 5 μg asbestos, was placed on a special multielectrode alignment grid and aligned.

After drying, the fibers were sprayed with parlodion solution (∿ 2% in amyl acetate), so that a thin parlodion film would be formed on the substrate. This film which contained all the fibers was then floated off on water and mounted on a plastic ring.

This ring was mounted perpendicular to a broad, collimated x-ray beam (see Fig. 1). The diffracted beam was measured at the 2θ angle corresponding to the (002) planes of chrysotile. The scattered beam was measured at the same angle but away from the diffraction direction. The instrument used in our research, although conceptually similar to that shown in Fig. 1, used only a single detector. Therefore, instead of a simultaneous measurement, the signal and background were measured sequentially with the sample rotated 90° between the measurements.

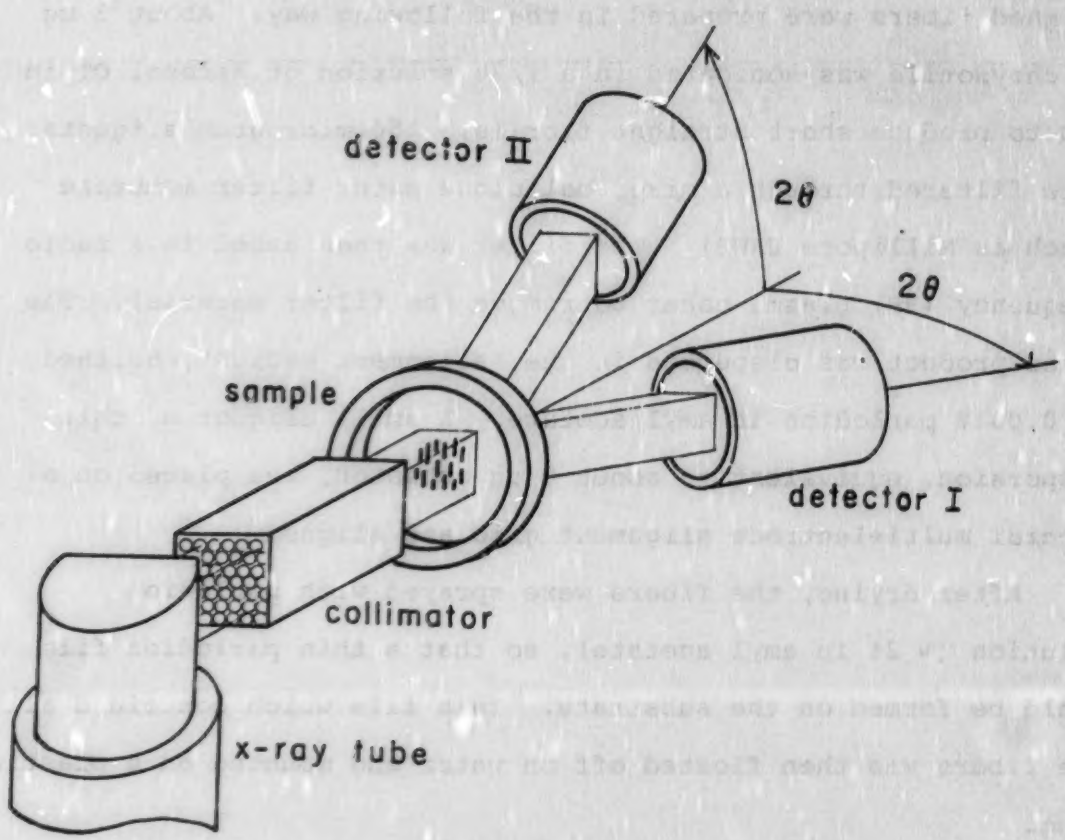


Figure 1. Double-detector instrument for x-ray diffraction measurement of aligned asbestos fibers. Detector I measures diffracted beam from aligned fibers; detector II measures the background corresponding to the same area on the sample.

6. SIGNIFICANT PARAMETERS IN SAMPLE PREPARATION

In the preparation of aligned standards, two potential problems had been recognized which were discussed in Ref. 1 and subsequent papers (Refs. 3, 4). One was the presence of extraneous material which accompanies any field-collection. The other was the fact that one could expect only a small total amount of asbestos in any reasonable-time collection requiring that all of the sample (rather than an aliquot) would have to be processed, aligned and measured. Therefore, it would be necessary to consider the difficulties associated with the alignment of the fibers in more than a single drop of fluid, perhaps in the presence of extraneous particulate material.

In the course of investigating these two parameters we also encountered additional problems associated with sample preparation even for pure asbestos standards. For example, the presence of undispersed lumps of asbestos degraded the alignment. In addition, even in samples with very good apparent alignment there were unexplained variations in x-ray sensitivity. These problems and more were systematically attacked and, with one exception (namely, the ashing of small samples), were satisfactorily resolved.

The present report is an account of that investigation. The relevant parameters are discussed roughly in the order in which they appear in the sample preparation procedure of Ref. 1, except when it is necessary to change the order to preserve continuity of subject matter. The parameters discussed are the following:

A - Filter pore size, fibril size distribution and fiber retention.

B - Composition of alignment medium.

C - Alignment of large (∿ 100 μℓ) volumes.

D - Effect of humidity.

E - Radio frequency ashing of small samples and blank filters.

F - Contamination effects.

A. FILTER PORE-SIZE AND FIBER RETENTION

The effect of filter pore-size on fiber retention and subsequent x-ray sensitivity is more significant than initially thought. When good alignments were obtained (as judged by observing fibers through optical microscope) this factor alone could explain most of the fluctuation in x-ray sensitivity. Although our feasibility report suggested the use of 0.45 μm filters for sample preparation, extensive research on filtration parameters since that time showed that significant losses could occur depending on the fiber size distribution.

In the tests performed to relate the x-ray sensitivity to filter pore size, fiber size distributions were varied by changing the sonication time, keeping all other sonication parameters as nearly constant as possible. For each sonication time (i.e. fiber size distribution) identical masses of asbestos dispersed in H_2O-OT were passed through various pore-size filters. The three filters used were of 0.22 μm, 0.45 μm and 0.80 μm pore sizes. Each experiment was repeated to obtain statistically valid data. Otherwise, all samples were prepared in as identical a fashion as possible.

A measure of the relative mass of fibers retained by each filter is the x-ray sensitivity measured for an aliquot as described in the 1975 report (Ref. 1). Here, x-ray sensitivity is to be interpreted as counts per second per microgram of the asbestos mass used in the filtration step, rather than the mass present on the sample. Table 1 shows the variation of measured x-ray sensitivities for a given sonication time with various pore sizes. It also shows the variation of sensitivity as a function of sonication time for a given pore size.

TABLE 1. X-RAY SENSITIVITY VS SONICATION TIME AND FILTER PORE SIZE

Filter Pore-Size	Sonication Time		
	40 min.	60 min.	120 min.
0.22 μm	5.7 ± 0.7	5.3 ± 0.5	4.2 ± 0.3
0.45 μm	4.7 ± 0.4	4.0 ± 0.5	2.6 ± 0.3
0.80 μm	3.8 ± 0.5	2.5 ± 0.2	1.3 ± 0.4

The numbers in this table should be considered only relative to one another. At the time these measurements were made, some problems still remained due to the effects of contamination on ashing and the spreading of the aligned drops due to the lower-than-optimum ambient humidity (both of which are discussed later in this report). However, the numbers given here remain consistent among themselves, even though the sensitivity obtained for 0.45 μm filter and 40-minute sonication time did not approach the previously reported value of 5.9 c/sec-μg. Note that, following the remedies discussed later, a well aligned standard chrysotile sample

using a 0.22 μm filter is now expected to give a sensitivity of about 7.5 c/sec-μg using the same x-ray tube parameters.

B. COMPOSITION OF THE ALIGNMENT MEDIUM

The liquid in which the fibers are electrostatically aligned is the same liquid in which they are dispersed after the organic material has been ashed. In this sense, the primary purpose of the alignment medium is its capability to disperse the fibers of asbestos. It is commonly observed that asbestos fibers in general tend to flocculate when they are suspended in water and then are allowed to dry. Similarly, when ashed pure asbestos fibers are stirred in pure amyl acetate with the aid of the small tip of sonic cell disrupter, they appear to be dispersed during the mix, but quickly settle when agitation has stopped. However, the addition of a quantity as small as 10 ppm parlodion (cellulose nitrate) to amyl acetate will produce a marked difference in the suspension of fibers and their dispersion. It appears that parlodion, even at this low level acts as a surface-active agent suitable for chrysotile and other silicates in amyl acetate, just as aerosol OT is suitable for chrysotile in water. However, although aerosol OT is highly soluble in amyl acetate, this mixture has not been found effective as a dispersing agent.

Any concentration of parlodion in amyl acetate (up to 1 or 2%) could be used to disperse asbestos fibers. But the second requirement of the dispersing liquid is to provide the proper dielectric properties for electrostatic alignment. Many experiments were performed to establish the suitable range of parlodion concentration in amyl acetate. Additional tests were conducted on

a number of other liquids and solutions (such as alcohols, acetone, freons, polystyrene thinner, etc.) to check for their suitability both as dispersant and alignment medium. The final results indicated that the proper liquid is a 10-20 ppm solution of parlodion in distilled amyl acetate. The total amount of parlodion necessary for any dispersion depends somewhat on the number of fibers in the liquid. However, as an empirical rule, any standard asbestos concentration up to $\sim$ 1 µg/µℓ can be easily dispersed in the sclution specified above.

When the parlodion concentration is reduced much below 0.001% (10 ppm), many fibers may remain undispersed, while for concentrations much above 0.002% (20 ppm) the fiber alignment is destroyed as the liquid dries on the alignment stage.

C. ALIGNMENT OF LARGE VOLUMES

In the case of field samples, the total asbestos content may be so small that it will be necessary to process and align the entire collected filters. The ashed residue from such a filter is usually high, as the total particulate matter in air is typically about 200 $\mu g/m^3$.

Since complete separation of asbestos from such a mass is not practical, the ashed residue cannot be dispersed easily in 5-10 µℓ of liquid, but may require as much as 100 µℓ. Alignment of the fibers present in such a relatively large volume was expected to be more difficult than the single drop used for the standards. Two procedures were considered: one was the use of a container above the alignment electrode, to contain the fluid while the solvent evaporated with the voltage applied to the grid

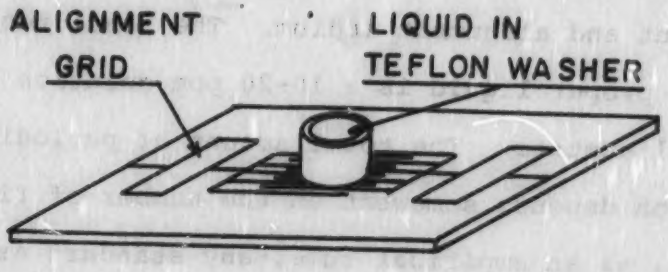


Figure 2. Test for feasibility of large volume dispersions. The small teflon cup is held in place by means of a clamp (not shown) to prevent the flow of liquid through the gap between it and the electrodes.

(see Fig. 2). This procedure was tested using teflon washers of different sizes. Although alignment was observed in most instances after evaporation, the major difficulty with the technique was the uncertainty in the amount of fibers lost due to the seepage of the liquid under the container, or due to their adherence to the walls of the container.

The second alternative was to align single drops sequentially on the same electrode until all the liquid was exhausted, allowing each drop to dry before the next is applied. This straightforward but tedious approach has proved more satisfactory. The reproducibility of sequential alignment can be shown by preparing pure asbestos dispersions diluted 10:1 and aligning 10 drops rather than 1. The x-ray sensitivities for three such samples are shown in Table 2.

TABLE 2. MULTI-DROP VS SINGLE DROP ALIGNMENT

TYPICAL X-RAY SENSITIVITIES

	Single drop 5 µℓ (4 µg)	Single drop 5 µℓ (0.4 µg)	Multi drop 50 µℓ (4 µg)
1	8.2	7.3	7.7
2	7.7	6.4	7.9
3	6.9	8.6	7.7

Sequential multi-drop alignment is obviously more time consuming per se than single drop operation. However, with careful planning this step can be performed without significantly influencing total time necessary for sample preparation when dealing with multiple specimens.

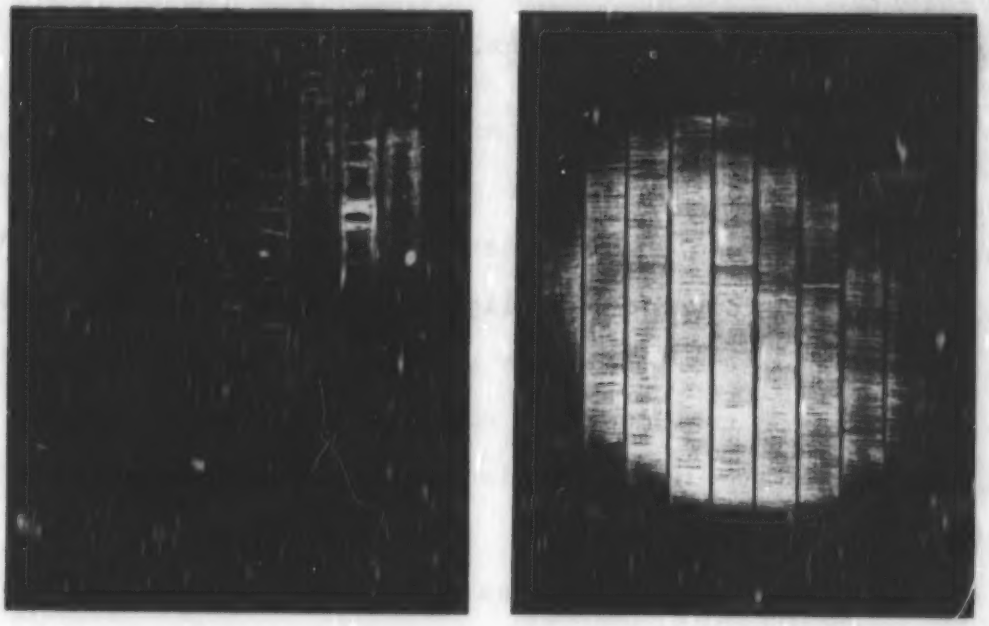
D. EFFECT OF HUMIDITY ON ALIGNMENT

The effect of humidity on alignment was discovered when it was noted that samples of asbestos which had been ashed and aligned in one test did not align at a later date, even though presumably the same conditions had been used. After considerable experimentation two important conclusions were drawn which related the humidity in the ambient environment to the quality of alignment:

1 - At very low humidities (e.g., 20% RH at 18° C), fiber alignment is very poor, regardless of the ashing conditions or parlodion concentration. As the humidity is raised to ∿ 40% RH at 20° C, the quality of alignment (containment of the drop in a small area, fiber orientation) reaches an optimum level.

The quality of alignment may be judged from the visual appearance of the aligned drop. Under good conditions, the fibers remain confined to the area covered by the drop at the moment of its impact on the grid, although the liquid itself may spread unevenly over the surface. Under poor conditions (such as low humidity) the spread of the liquid also carries with it the suspended fibers, most of which may collect at the boundary of the drop, unaligned (Figs. 3A, B).

To demonstrate the effect of ambient humidity the following alignments were conducted. Sample A was a 5 µℓ drop aligned in the ambient humidity of 25% (20° C). Sample B was a drop of the same specimen, which, after deposition on the grid, was exposed



(A) (B)

Figure 3. Appearance of alignment under (A) poor and (B) proper relative humidity. The effect of humidity is to "lock in" the fibers in an area determined by the drop at the moment the power is turned on.

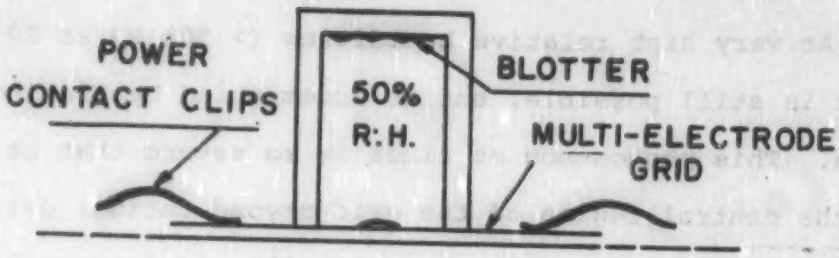


Figure 4. Apparatus to establish correlation between humidity and alignment. A small inverted cup (approximately 25 mm in diameter and 30 mm high) over the electrodes contains a circle of blotter paper, moistened just enough to raise the relative humidity inside to about 50%. Only a short exposure (1-2 seconds) to the drop is needed, after the power is turned on, to yield Figure 3B.

for 1-2 seconds to a small inverted cup (Figure 4) conditioned to an RH of 50%. The striking difference between the samples was not only seen qualitatively, as described above, but also in the x-ray sensitivities: 2-4 c/sec-μg for 25% RH, 6-7 c/sec-μg for 50% RH. Similar values were obtained consistently for many more samples tested for this variable (Table 3).

TABLE 3. DEPENDENCE OF X-RAY SENSITIVITY ON AMBIENT RELATIVE HUMIDITY

Sample #	RH 20-30%	RH 40-50%
1	2.3	6.0
2	3.2	6.9
3	4.3	6.4
4	4.6	7.3

2 - At very high relative humidities (> 50% RH at 20-22° C) alignment is still possible, but is accompanied by electrode corrosion. This phenomenon at times is so severe that it will destroy the central region of the grid beyond further use. Some degree of accidental corrosion is tolerable, as long as it leaves most of the electrodes continuous and intact. Slight non-uniformities in the electrodes' profile have had no detectable effect on the future alignments or on the x-ray sensitivities. Grids seriously corroded during alignment have caused samples to be more difficult to float off the electrode (even when the electrode had been corroded slightly during previous use) possibly because of the adherence of the corrosion product to the quartz substrate.

The optimum humidity condition for alignment has been determined to be 40-45% RH at 20-22° C. Extremes, such as 50% RH at 23-25° C, or 25% RH at 18° C should be avoided altogether.

E. R-F (RADIO FREQUENCY) PLASMA ASHING

The conditions required for proper ashing were investigated on the basis of the observation that the lower the quantity of ashed residue, the better the overall quality of the final aligned sample. Proper ashing is dependent on several inter-related factors.

a - Instrumental factors: RF level, vacuum conditions, gas flow, geometry.

b - Filter conditions: filter types and "loading", i.e., the amount and type of material present; filter exposure to RF field, etc.

c - Contamination effects.

The ashing step is the most critical step in the sample preparation. Good fiber dispersion or alignment canot be expecteo unless each of the factors described above is strictly controlled.

Instrumental Factors

One of the first parameters to be studied was the geometry and the physical placement of the sample in the RF asher, i.e. the way in which filters and their load should be exposed to the RF plasma. The ashed material should be contained suitably for further redispersion in the H_2O-OT or dispersion in amyl acetate-parlodion (AA-P). Redispersion of ashed residue in H_2O-OT is necessary for field-sample collections which contain a finite level of soluble impurities, and which need washing and refiltration. Dispersion in AA-P is for alignment of clean standard samples, and for samples ashed after redispersion in H_2O-OT.

In either case, it is necessary to contain the ashed product in a small volume such as a test tube, so that the final dispersion volume in AA-P can be small. This is true, because in the case of the source sample, all of the liquid must be aligned drop by drop, and hence the total elapsed time for a complete sample alignment depends on the volume of the liquid.

Confinement of the filter in a test tube, however, raises a question about the variation in the amount of RF exposure to different samples. An optimum length for the test tubes was found suitable for our asher (Perkin-Elmer Coleman 40 - not available any longer commercially). Ordinary culture tubes (10 x 75 mm)

are cut to 25 mm length and cleaned. The filters are then folded by tweezers and inserted in these tubes. Short tubes were found to be more satisfactory than the original long tubes, because the latter increased the time required for complete ashing.

The Coleman RF asher has no provision for measuring the power being input to the samples. By comparing the results of ashing samples in other instruments (through the courtesy of the Electronics Division, NRL and NASA, Goddard), it can be estimated that ashing six samples requires about 10-20 watts of RF power. An oxygen flow of 10 cc/min through a 4-cm diameter reaction chamber has been established to give optimum results under vacuum of 0.5-1 torr.

One ashing practice for electron microscopy is to attach the filter onto a glass slide using a few drops of acetone. The glass slide is then inserted in the reaction chamber, and exposed to RF plasma. We found this procedure unsatisfactory; in most cases the filter began peeling from the slide soon after vacuum pumpdown started in the chamber. The ashed product lay loosely atop the glass slide, and sample loss occurred when air was allowed in the system. Only in those cases where the glass slide was purposely contaminated with finger dirt, etc., did the filter adhere to the glass throughout the ashing operation. This, however, would yield a product not only unsuitable for alignment but for electron microscopy as well.

In other instances when the sample is on a slide, it has been observed that the filter material flashes out spontaneously, scattering fibers irretrievably in the reaction chamber. This is another reason why containment of the ashed product in a test tube is the only way to proceed.

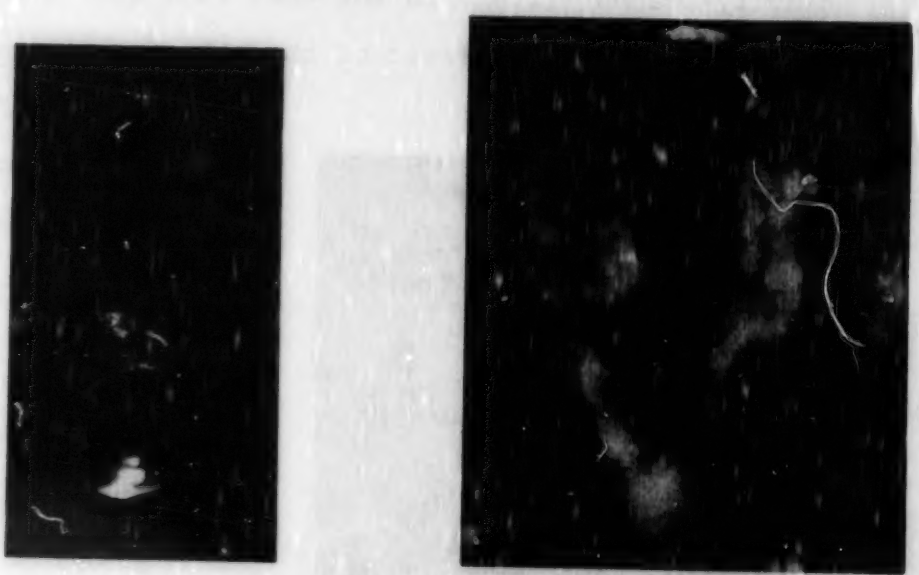
Filter Condition: Relationship Between Load Level and Ashing

A peculiar aspect of the ashing process concerns the amount of ashed filter residue, when filters containing small amounts of pure asbestos ($\lesssim$ 1 µg/cm^2) are compared to filters with large quantities of material (5-70 µg/cm^2). In the feasibility report (1975), a description was given for sample preparation, when quantities as large as 150 µg asbestos ($\sim$ 75 µg/cm^2) were filtered, ashed, and dispersed in AA-P. From these samples, small (5 µg) aliquots were placed directly on the alignment grid and aligned. Observation of these samples by optical and electron microscopy revealed very little extraneous matter, so that the ashed residue of the filter itself was presumed to be negligible. Ashed, heavily-loaded filters in the test tube have a distinct translucent appearance, characteristic of the asbestos fibers themselves. The ashed filter "copies" the outline of the area filtered from H_2O-OT dispersion. In general, there appears to be no visible residue from the filter itself (Figure 5).

Figure 5. Appearance of an ashed filter containing a large (150 µg) quantity of standard asbestos. Note in particular the shape of the asbestos sheet at the boundary of filtration area.

On the other hand, the preparation of a field sample (collected near or at an emission source) may involve the ashing of a "lightly-loaded" filter, i.e., a filter with only 1-2 µg (0.5-1.0 µg/cm^2) asbestos. Here, the entire filter must be ashed and aligned. Either blank, or lightly loaded filters (with pure standard asbestos) have shown erratic results in appearance and amount of ashing residue.

The ashing of a blank filter often results in a solid plasticized mass at the bottom of the test tube (Figure 6A). No reasonable level of sonication in AA-P will break or disperse this mass, which, incidentally, is denser than the liquid and will not remain suspended (Figure 6B).



(A) (B)

Figure 6-(A). An ashed blank filter in test tube (3x). (B) Optical micrograph (500x) of the filter dispersed in AA-P and "aligned" to show undispersed lumps and their chaining in the field.

Figure 7. Lightly-loaded filter, ashed and dispersed in AA-P, showing large particles which distort the alignment field.

Filters with small amounts of asbestos have also shown the same general effect, in contrast to heavily-loaded samples. Dispersions of these samples under optical microscope show masses of transformed matter many tens of microns in diameter, each containing a small fraction of the fibers (Figure 7). Alignment of such samples almost invariably leads to a chaining together of the masses, distortion of the field near the few free fibers and a nearly zero sensitivity.

A comparison of lightly-loaded and heavily-loaded filters seems to indicate that the large quantity of interwoven asbestos fibers acts as a supporting grid to allow the filters to ash slowly and completely. Most of the incomplete or poor ashing appears to be the result of the filter collapsing and rolling onto itself - thereby preventing complete interaction with the plasma.

This suggests the idea of preloading the filter with an inert fibrous material which would not interfere with the x-ray measurements. For example, when the measurement of chrysotile or amosite is intended, a suitable quantity of the crocidolite could be added to the samples. The diffraction peak from crocidolite is at about 14° 2θ (Cr Kα radiation) which is sufficiently removed from both chrysotile (18°) and amosite (16°). Also under consideration at the present time is the use of polyester-reinforced mixed cellulose ester filter membrane. Polyester is highly resistant to ashing and may therefore support the filter throughout ashing and prevent it from collapse. After ashing, it may be shaken off with sonication in H_2O·OT. During the second ashing, a much smaller filter could be used to minimize the volume of the alignment liquid. An advantage of the smaller filter disks (e.g. 8 mm) is that the load concentration is increased to the point that the filter disk may be more completely ashed due to the load support (see discussion below).

In most sampling situations, however, preloading automatically occurs due to the presence of extraneous particulate matter: If a cubic meter of air is collected, then it is likely that about 100-200 µg extraneous material may also be present on the filter. This quantity seems to be just the proper level of filter support for good ashing.

An attempt has been made to increase the concentration of asbestos on the filter membrane by reducing the filtration area. Consider the case of pure chrysotile. Ashing a 16 mm filtration disk has been observed to be successful for a load level of $\sim$ 10 µg (5 µg/cm^2). Therefore, it would seem reasonable that a

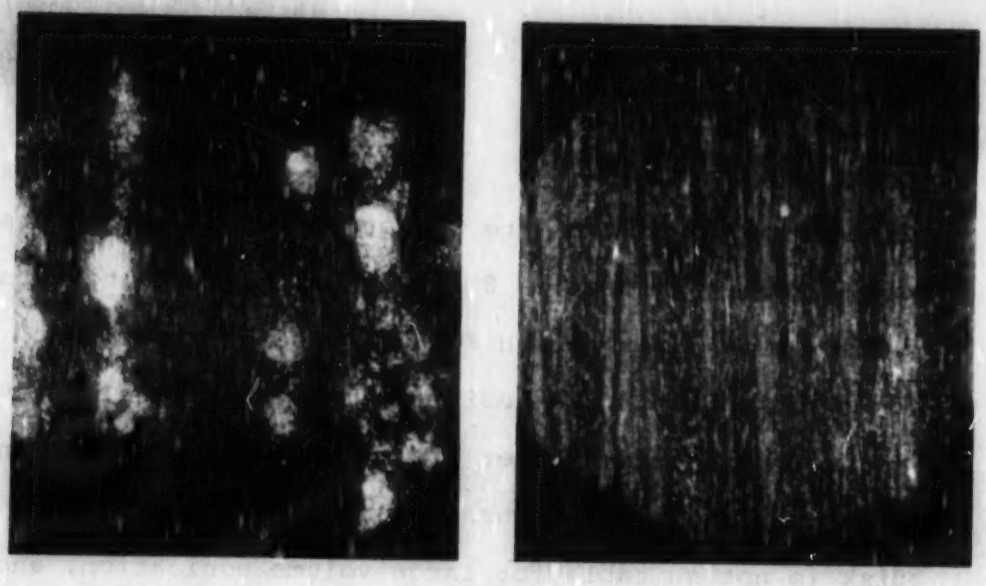
Figure 8. Improvement in the ashing quality of small (8mm) filter disks (3x). This test tube contained about 4 µg total asbestos, and should be compared with Figures 5 and 6.

load level of 2.5 µg pure asbestos with no extraneous matter would require a disk of 8 mm in diameter. To test this idea, 8-mm upright filteration funnels were fabricated and used to filter 2.5-3 µg asbestos. A definite improvement was observed in the ashing quality of smaller disks (Figure 8) approaching that shown for larger samples (Figure 5). However, it is clear that such a disk is not suitable for large volume sonication, and its use may be limited to the re-ashing of the second filtration.

F. CONTAMINATION EFFECTS

At least part of the problem of poor ashing may be related to the contamination of the filter itself. For example, the spacer used in the packaging of the filter membranes may become suspect. The presence of impurities in the filter may act to at least locally affect the quality of ashing. To ascertain whether this

impurity played a major role in the alignment, several filter membranes were acid cleaned to dissolve away impurities. Filters were then washed, dried, and used for filtration of standard asbestos. (Some warping of the membrane occurs after acid bath and washing.) Experiments with these filters, however, showed no significant improvement in the fiber dispersion or ashing of blank filters. However, with some ashings, it is even possible to detect the operator's fingerprint on the ashed asbestos sheet.



A B

Figure 9A. Appearance of non-alignable bundles of fibrils (500x photomicrograph). For comparison, fully dispersed, aligned fibers are shown in 9B.

Other tests on the presence of impurities were conducted. For example, the presence of a very thin (∿ 1-2 μm) layer of ferric sulfate or silver chloride on the filter greatly dimishes the ashing rate and thus contributes to the later contamination of the alignment medium, through dissolution of the filter membrane in amyl acetate. This contamination can destroy electrostatic alignment.

Another contamination problem, distinct from, but similar to the incomplete ashing of blank filters, is traced to the use of undistilled but deionized water. Lumps of asbestos fibrils appear to remain intact after an otherwise complete ashing. Under optical microscopic examination, they appear as granular portions of unashed filter (Figure 9). Even after extensive sonication and experimental changes in parlodion concentration, they remain fairly intact, and the alignment of fibrils as well as x-ray sensitivity is affected by their presence. However, electron microscopy shows that each "granule" is composed of straight, short fibrils held together with a minute amount of adhesive-like material (Figure 10). The exact nature of the adhesive has not been determined. However, it is interesting to observe the sharp boundary between fiber and no-fiber region. It indicates that the nature of this impurity is local and is probably brought about as a result of the decomposition of the impurity into a non-ashable, insoluble compound. The impurity finds its way through the ion-exchanger column, and may be trapped only by the small pores of the filter membrane.

The use of distilled water, or deionized, distilled and filtered water seems to eliminate this difficulty, and again is emphasized throughout the sample preparation.

Figure 10. Electron micrograph (5000x) from bundles in sample of Figure 9A. Unlike the photomicrograph, the boundaries of lumps appear quite sharp.

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